Fractional impurity moments in two-dimensional non-collinear magnets

Alexander Wollny,[1] Lars Fritz,[1] and Matthias Vojta[2]

[1] Institut für Theoretische Physik, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany
[2] Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany

(Dated: January 20, 2013)

We study dilute magnetic impurities and vacancies in two-dimensional frustrated magnets with non-collinear order. Taking the triangular-lattice Heisenberg model as an example, we use quasi-classical methods to determine the impurity contributions to the magnetization and susceptibility. Most importantly, each impurity moment is *not* quantized, but receives non-universal screening corrections due to local relief of frustration. At finite temperatures, where bulk long-range order is absent, this implies an impurity-induced magnetic response of Curie form, with a prefactor corresponding to a *fractional* moment per impurity. We also discuss the behavior in an applied magnetic field, where we find a singular linear-response limit for overcompensated impurities, and propose experiments to test our theory.

Impurities have been established as a powerful means to both probe and tune bulk properties of correlated-electron materials. In quantum magnets, non-trivial phenomena include vacancy-induced magnetism in quantum paramagnets [1] and quantum percolation [2]. Single-impurity behavior has been predicted to be exotic in quantum critical magnets, where a universal fractional Curie moment appears at low temperatures [3–5]. Isolated impurities in magnets with long-range order have been studied as well, with most works focussing on the square-lattice Heisenberg magnet [3, 4, 6, 7].

This paper is devoted to impurities in geometrically frustrated spin-S magnets which order non-collinearly – a topic which has received little attention [8]. As we show below, vacancies (i.e. non-magnetic impurities) in non-collinear magnets display a behavior which is richer and qualitatively different compared to their collinear counterparts. In particular, the magnetic moment m associated with a single vacancy is *not* quantized, in contrast to the collinear case [3] where it is locked to $m = S$. This effect is already present at the classical level: nearby spins re-adjust their directions in response to the vacancy, reflecting that frustration is locally reduced. This partially screens the vacancy moment, with the screening cloud decaying algebraically due to Goldstone modes.

At zero temperature, the direction of the vacancy moment m is fixed by the bulk magnetic order. In contrast, at $T > 0$ in two dimensions (2d) there is no long-range order due to the Mermin-Wagner theorem, and the vacancy moment is free to rotate. This rotation is classical, as it is coupled to a rotation of the bulk spins surrounding the vacancy [3, 4]. As a result, the linear-response susceptibility has a singular piece, $\chi_{\rm imp}(T) = m^2/(3kT)$, corresponding to the Curie response of a *fractional* moment for each vacancy [9]. For the triangular-lattice Heisenberg antiferromagnet (AF) with nearest-neighbor interactions, we find in a $1/S$ expansion

$$m = -0.040S + 0.196 + \mathcal{O}(1/S) \;, \qquad (1)$$

where a negative sign corresponds to overcompensation, described in detail below. In stark contrast to fractional effective moments found at bulk or boundary quantum critical points [3, 5, 10], the present mechanism is realized deep inside the renormalized classical regime [11] of a 2d magnet.

A finite magnetic field h has two effects which tend to compete: it orients the impurity moment parallel to the field and it induces a macroscopic bulk moment. This bulk–boundary competition is governed by a field-induced length scale $l_h \propto 1/h$ and limits the linear-response regime [12]. For a single overcompensated impurity in the triangular lattice, we find this competition to be particularly drastic: Linear response breaks down at any finite field.

In the body of the paper, we sketch the derivation of these results and propose tests and extensions of the non-trivial screening advocated here. Our considerations qualitatively apply to a large class of frustrated AFs with non-collinear ground states, which are unique up to global spin rotations. For definiteness, we will present results for the spin-S triangular-lattice Heisenberg model

$$\mathcal{H} = \sum_{\langle ij \rangle} \left[J\vec{S}_i \cdot \vec{S}_j + K(\vec{S}_i \cdot \vec{S}_j)^2 \right] - h \sum_i S_i^z. \qquad (2)$$

The biquadratic exchange, with its strength parameterized by $k = K/(JS^2)$, generates a family of models and, in particular, lifts the accidental classical degeneracy of the simple nearest-neighbor Heisenberg model in an applied field [13]. In zero field, the ground state is given by the familiar coplanar 120° ordering at wavevector $\vec{Q} = (4\pi/3, 0)$ for $-2/9 < k < 2/9$.

Vacancy in the ground state of a classical non-collinear magnet. Consider a bulk AF with geometric frustration, where not all energetic constraints (e.g. all neighboring spins pairwise antiparallel) can be satisfied. Removing a single spin locally reduces frustration due to the elimination of constraints. For a non-collinear magnet, this seeds a re-adjustment of spin directions.

For the triangular lattice, this re-adjustment is illustrated in Fig. 1a, which shows the result of a numerical

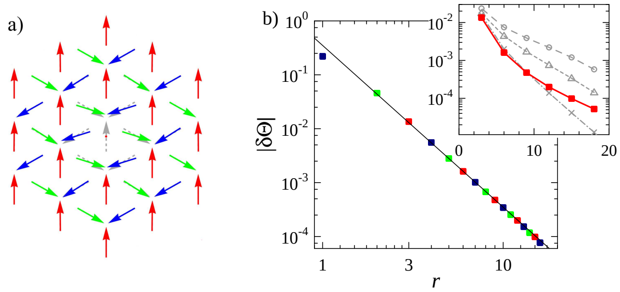

FIG. 1: a) Classical ground-state spin configuration of the triangular AF with vacancy, showing the spin re-adjustment near the vacancy; the dashed arrows indicate the original 120° order. b) Rotation angle $|\delta\Theta|(r)$ along a high-symmetry line for $k = 0$ and $L = 51$, together with the asymptotic power law $\delta\Theta \propto 1/r^3$. The inset shows the same data (solid), together with $|\delta\Theta(r)|$ at finite field $h/J = 0.5$ (dashed), 1.0 (short dash), 1.5 (dash-dot), all for $k = -0.05$, for one sublattice in a log-linear plot. The exponential (instead of power-law) decay for $h > 0$ is obvious.

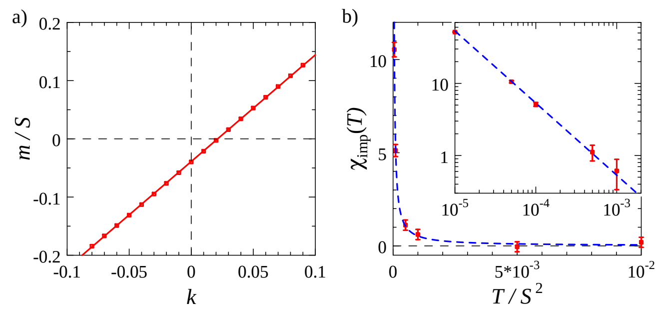

FIG. 2: a) Effective vacancy moment m/S for the classical triangular Heisenberg AF as function of the biquadratic exchange k in Eq. (2). b) MC results for $\chi_{\rm imp}$ as function of T/S^2, calculated with $JS^2 = 1$ and $k = 0$. The dashed line shows the predicted Curie law $m^2/(3kT)$ (3) with $|m/S| = 0.04$. The inset shows the low-temperature data in a log-log plot. The data in a (b) have been obtained for systems of size $L = 51$ ($L = 9, 12$); finite-size effects are negligible.

optimization of the spin directions in a finite system of size L^2 with $L = 51$, where a single spin has been removed. The spins remain coplanar and rotate by angles $\delta\Theta$ relative to the original 120° configuration, such that the spins near the vacancy tend to be more antiparallel. The numerical results for $\delta\Theta$ show a sixfold (f-wave) angular symmetry and are consistent with a spatial decay of $\delta\Theta(r) \propto 1/r^3$, Fig. 1b [8].

This result is rationalized as follows: The full rotation pattern can be understood as the response of the system to a field $\tilde{h}$ which couples to the six neighbors of the vacancy such that these spins are rotated towards an antiparallel configuration. Hence, the field $\tilde{h}$ acting on these six sites is locally transverse and alternating, in a rotated frame compactly written as $\tilde{h}\sum_{j=1}^{6}\beta_j S_j^x$ with $\beta_j = (-1)^j$. The long-distance rotation is determined by a transverse susceptibility, which is dominated by the modes near the ordering wavevector with linear dispersion ω_q. A straightforward calculation gives $\delta\Theta(r) \propto \int d^dq e^{i\vec{q}\cdot\vec{r}}\beta_q/\omega_q^2 \propto 1/r^{d+1}$.

The state with a single vacancy has a finite magnetization m. While this would simply be $m = S$ without re-adjusted angles (i.e. in the collinear case), the re-adjustment tends to screen this moment. For the triangular lattice, the numerical result, obtained from integration over the screening cloud, is $m/S = -0.0396(3)$, i.e., the missing spin is *over*compensated, such that the total moment points in the direction of the removed spin. The value of m is non-universal, i.e., depends on details of the Hamiltonian: Fig. 2a shows m/S as function of the biquadratic exchange coupling K in Eq. (2).

Vacancy: 1/S corrections. Quantum corrections to the classical $T = 0$ results can be obtained using spin-wave theory. Holstein-Primakoff bosons a are introduced to capture deviations from the classical state in the presence of a vacancy, Fig. 1a. Upon expressing the Heisenberg model in terms of the a bosons, terms linear in a vanish as required. Linear spin-wave theory amounts to a diagonalization of the quadratic-in-a piece of the Hamiltonian, which has to be done numerically for finite lattices [14] due to the inhomogeneous reference state. Doing so, we find the full spectrum of eigenvalues and eigenvectors, which can be used to calculate $1/S$ corrections to thermodynamic observables as well as response functions.

The local magnetization correction $\delta m(\vec{r}_i) = \langle a_i^\dagger a_i\rangle$ decays to the known bulk value of $\delta m_b = 0.26$ [15] at long distances, corresponding to a staggered magnetization of $m_b = S - 0.26$. The impurity contribution, $\delta m(\vec{r}_i) - \delta m_b$, indicates enhanced quantum corrections near the impurity which fall off as $1/r^3$, consistent with the Goldstone-mode expectation. The $1/S$ correction to the uniform moment associated with the vacancy is obtained from integration, $\delta m = \sum_i \delta m(\vec{r}_i)\cos\Theta(\vec{r}_i)$, which evaluates to $\delta m = 0.196$, Eq. (1). Further corrections at higher orders in $1/S$ will not qualitatively modify the result of a non-universal fractional value of m, but apparently both overcompensation and undercompensation may occur, depending on S and microscopic details. We note that local impurity-induced magnetization corrections obeying $\delta m(\vec{r}_i) - \delta m_b \propto 1/r^3$ also occur in the collinear square-lattice case, but here spin conservation demands that the integral δm vanishes; hence m remains locked to S [4, 6].

Finite temperatures: Fractional Curie response. For $T > 0$ in two space dimensions, long-range bulk magnetic order is destroyed by thermal fluctuations, with the correlation length ξ being exponentially large at low temperatures, $T \ll J$. Consequently, the direction of the impurity moment is no longer fixed, but is free to rotate with the local orientation of the bulk magnetic domain surrounding the impurity. It has been shown both an-

alytically [3, 4] and numerically [7] that this rotation is classical and leads to a linear response of Curie form:

$$\chi_{\rm imp}(T) = \frac{m^2}{3kT} + \mathcal{O}(T^0) \,, \tag{3}$$

where the subleading term receives a multiplicative logarithmic correction in 2d [4, 7, 16].

In the non-collinear case, the partial screening of the vacancy moment, established above for $T = 0$, will remain intact at small $T > 0$ because of the large correlation length. This implies a Curie response (3) corresponding to a fractional moment per vacancy. This central result is fully borne out by numerics: we have performed classical Monte Carlo simulations of triangular-lattice Heisenberg magnets, using the standard Metropolis algorithm. In Fig. 2b we show the result for the impurity susceptibility $\chi_{\rm imp}$, obtained from subtracting the linear-response χ of a system with vacancy from that of a system without vacancy. While the high-temperature part is difficult to analyze given the error bars, the low-temperature data clearly show a Curie divergence, with a prefactor consistent with $|m/S| = 0.04$ within error bars. For $S < \infty$, we expect a subleading $\log T$ contribution to $\chi_{\rm imp}(T)$ arising from Goldstone modes similar to the collinear case; a detailed analysis will appear elsewhere.

Vacancy vs. extra spin. So far, we have considered the special case of a vacancy, experimentally obtained by replacing a magnetic by a non-magnetic ion. A different type of impurity is an extra spin of size S', coupled to a single site of the bulk magnet with a Heisenberg coupling J'. For antiferromagnetic $J' \gg J$ and $S = S'$, the impurity spin and its bulk partner lock into a singlet, and we recover the vacancy case. On the other hand, for $J' \ll J$ the re-adjustment of the spin directions due to the impurity will be parametrically small in J'/J, and we expect for the impurity moment $m \to S$ as $J' \to 0$. Hence, varying J'/J leads to a continuous change of m. Interestingly, this crossover *cannot* be captured in a $1/S$ expansion for the extra-spin problem: In the classical limit, there is no singlet formation for large J', and this is not recovered at any order in $1/S$, as can be seen by explicit calculation. However, the direct vacancy calculation *can* be performed in $1/S$, as shown above, the crucial difference being that the missing spin (or the $J' = \infty$ singlet) is built in from the outset.

Finite magnetic field. For the collinear square-lattice AF, it has been shown that a vacancy in a finite applied field generates spin textures in its vicinity, which result from the competition between aligning the vacancy moment and inducing a bulk moment [12]. Here we investigate the non-collinear case on the triangular lattice. As the nearest-neighbor Heisenberg model has an accidental degeneracy of classical ground states at finite fields, which is lifted in favor of coplanar states (Fig. 3a) both by quantum and thermal fluctuations [17, 18], we choose to investigate the classical model with biquadratic exchange, Eq. (2) with $-2/9 < k < 0$, which leads to the same coplanar finite-field phases as the ones selected by fluctuation effects. (Non-coplanar states are favored for $0 < k < 2/9$.)

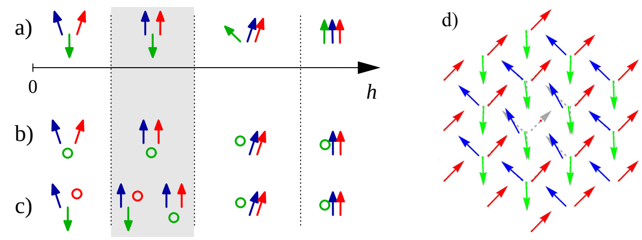

FIG. 3: a) Schematic evolution of the three-sublattice coplanar bulk spin configurations as function of applied field for the triangular AF, with the 1/3 magnetization plateau shaded. These states are selected out of the classical $k = 0$ ground-state manifold of $\mathcal{H}$ (2) by both thermal and quantum fluctuations as well as negative small k. A single vacancy chooses one of the sublattices: b) undercompensated and c) overcompensated case. In b), an impurity quantum phase transition occurs inside the plateau phase. (Note that undercompensation does not occur in our family of classical models with $k < 0$, but is expected for $S < \infty$ from Eq. (1).) d) Spin configuration with (overcompensated) vacancy, calculated for $h/J = 1.0$, $k = -0.05$, and $L = 51$.

Qualitatively, the vacancy physics strongly differs between the undercompensated and overcompensated cases. For undercompensation, Fig. 3b, a small field will orient the system such that the vacancy sublattice points antiparallel to the field. This is compatible with the field-induced bulk state, hence a strong competition between bulk and boundary effects is absent, and the zero-field limit will be smooth.

This is different in the overcompensated case, where orienting the vacancy moment in field direction is *incompatible* with the bulk state. Our numerics shows that the system chooses a compromise such that the vacancy sits in one of the sublattices directed approximately parallel to the field, with a significant distortion near the vacancy, Fig. 3c,d. This distortion falls off exponentially (there is no coupling to the remaining Goldstone mode), with a length scale $l_h \propto 1/h$ [12], Fig. 4b. Most importantly, the zero-field limit is *singular* in this case, i.e., the distortion pattern for $h \to 0$ does not recover its zero-field structure. This is seen in both the inset of Fig. 1b and Fig. 4a. The latter shows $m_{\rm imp}(h)$, defined as the difference of the total magnetizations with and without vacancy. By construction, $m_{\rm imp}(h=0) = |m|$ and $m_{\rm imp}(h \to \infty) = -S$. Fig. 4a demonstrates that $m_{\rm imp}(h \to 0)$ again represents a fractional impurity moment which is different from $|m|$ in the overcompensated case.

The evolution of $m_{\rm imp}(h)$ through the bulk magnetization plateau is also very different in the undercompensated and overcompensated cases, Fig. 3b,c. While it is smooth for undercompensation, a jump occurs at $h = 3J$

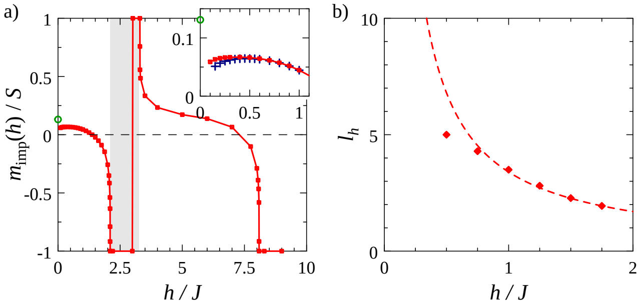

FIG. 4: a) Impurity contribution to the magnetization, $m_{\rm imp}(h)/S$, as function of applied field h, for the classical triangular AF (2) with $k = -0.05$. The shaded region corresponds to the bulk 1/3 magnetization plateau. The inset shows a zoom onto the small-field region; squares (crosses) are data for $L = 51$ ($L = 21$). The circle at $h = 0$ represents the linear-response value $|m/S|$, demonstrating the breakdown of linear response for this overcompensated case. b) Field-induced length scale $l_h(h)$ obtained from an exponential fit to $\delta\Theta(r)$ for $L = 51$, together with the anticipated $l_h \propto 1/h$ behavior (dashed). Finite-size effects are important for small $h > 0$ where $l_h \ll L$ is violated.

in the overcompensated case, Fig. 4a. This signals a first-order impurity transition where the vacancy site switches the sublattice implying that the entire bulk configuration rearranges.

Finite impurity concentration. We finally discuss the measurable consequences of our findings in the realistic case of a finite impurity concentration $n_{\rm imp}$. Assuming that the impurities are distributed equally over all sublattices, their moments tend to average out at $T = 0$ and $h = 0$. This behavior persists at finite T, provided that $\xi \gg l_{\rm imp}$ where $l_{\rm imp} = n_{\rm imp}^{1/d}$ is the mean impurity distance. In the opposite limit, $\xi \ll l_{\rm imp}$, the impurity moments fluctuate independently, and their response simply adds up. Hence, observing fractional Curie response of independent impurity moments is possible at elevated T and small $n_{\rm imp}$ [9]. Note that elevated fields which induce $l_h \ll l_{\rm imp}$ also lead to an effective decoupling of multiple impurity moments, which, however, are polarized in this limit. The spin re-arrangement predicted to occur inside the plateau phase for overcompensated impurities is detectable by local probes like NMR.

Conclusions. For impurities in non-collinear magnets, our main result is a partial screening of the impurity magnetic moment, leading to a fractional Curie response at low temperatures in the 2d case. We have evaluated the vacancy moment for the spin-S triangular-lattice AF in a $1/S$ expansion, but we expect our qualitative results to be valid for any frustrated AF with non-collinear ground state (which is unique up to global spin rotations).

Our predictions could in principle be verified by large-scale numerical studies in analogy to Refs. [5, 7], however, quantum Monte-Carlo approaches are plagued by the sign problem which is serious for most frustrated AF. On the experimental side, one can expect the physics described here to be generically realized, as Curie tails in $\chi(T)$ due to impurities are routinely observed in magnets. A *quantitative* analysis of these tails in samples with known concentration of impurities would allow to extract the fractional moment size m (in a regime where interactions between the impurity moments are small); our prediction is $m \ll S$ in contrast to the behavior in collinear magnets.

An interesting open question is how the fractional moment advocated here evolves upon approaching a quantum critical point of the bulk magnet, where *at* criticality a universal fractional response is expected. Our results also call for investigations of vacancies in frustrated collinear magnets where vacancies may induce non-collinear spin textures in order to reduce frustration.

We thank R. Moessner, A. Rosch, Q. Si, and O. A. Starykh for illuminating discussions. This research was supported by the DFG through SFB 608 (Köln) and GRK 1621 (Dresden). MV also acknowledges financial support by the Heinrich-Hertz-Stiftung NRW and the hospitality of the Centro Atomico Bariloche.

[1] J. Bobroff *et al.*, Phys. Rev. Lett. **103**, 047201 (2009) and references therein.
[2] A. W. Sandvik, Phys. Rev. Lett. **96**, 207201 (2006); T. Vojta and J. A. Hoyos, preprint arXiv:0707.0658.
[3] S. Sachdev, C. Buragohain, and M. Vojta, Science **286**, 2479 (1999).
[4] S. Sachdev and M. Vojta, Phys. Rev. B **68**, 064419 (2003).
[5] K. H. Höglund and A. W. Sandvik, Phys. Rev. Lett. **99**, 027205 (2007).
[6] O. P. Sushkov, Phys. Rev. B **68**, 094426 (2003).
[7] K. H. Höglund and A. W. Sandvik, Phys. Rev. Lett. **91**, 077204 (2003).
[8] Vacancies in a triangular magnet were briefly discussed in: C. L Henley, Can. J. Phys. **79**, 1307 (2001), but we believe the statement about the $1/r^d$ power-law decay of the rotation angle near the vacancy to be incorrect.
[9] Practically, the Curie response will be cut-off by interactions between the vacancy moments and by spin anisotropies leading to bulk order at finite T.
[10] M. Vojta, Phil. Mag. **86**, 1807 (2006).
[11] S. Chakravarty, B. Halperin, and D. R. Nelson, Phys. Rev. B **39**, 2344 (1989).
[12] S. Eggert *et al.*, Phys. Rev. Lett. **99**, 097204 (2007).
[13] A. Läuchli, F. Mila, and K. Penc, Phys. Rev. Lett. **97**, 087205 (2006).
[14] We employ the algorithm described in the appendix of: S. Wessel and I. Milat, Phys. Rev. B **71**, 104427 (2005).
[15] A. L. Chernychev and M. E. Zhitomirsky, Phys. Rev. B **79**, 144416 (2009)
[16] N. Nagaosa, Y. Hatsugai, and M. Imada, J. Phys. Soc. Jpn **58**, 978 (1989).
[17] A. V. Chubukov and D. I. Golosov, J. Phys.: Condens. Matter **3**, 69 (1991).
[18] H. Kawamura and Y. Miyashita, J. Phys. Soc. Jpn. **54**, 4530 (1985).